Inkjet Printing of Well-Adapted PEDOT-PSS Dispersions

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Abstract

Poly (3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT-PSS) is a popular conductive polymer that finds widespread use in the fields of polymeric electronics and display applications. Its major advantages lie in the suitability for flexible electrical devices and the relatively simple deposition process capabilities with techniques such as inkjet printing. However, the deposition of PEDOT-PSS dispersions with inkjet printheads can cause a number of problems due to possible interaction of the fluids with the printhead, and due to poor inkjet functionality and layer formation on the substrate. In the present work we have adapted PEDOT-PSS dispersions for improved performance in a Xaar-type piezoelectric inkjet printhead, in particular for high quality drop formation and for reduced corrosion of the inkjet printhead. At the same time the best PEDOT-PSS inks regarding layer formation and conductivity were identified. As an application example, a passive LCD device incorporating an inkjet printed PEDOT-PSS electrode pattern that was produced with an adapted PEDOT-PSS ink is presented.

Introduction

With the increasing popularity of flexible organic electronics and displays over the past years, there has been a growing interest in conductive polymeric materials. Poly (3,4-ethylenedioxythiophene)-polystyrenesulfonic acid (PEDOT-PSS) is such a conductive polymer that already finds use in commercial applications, due to its good conductivity and transparency. Although the values for these parameters cannot presently compete with indium tin oxide (ITO), widely used as electrode materials in display applications, there are advantages of PEDOT-PSS in being easily processed and being mechanically flexible. PEDOT-PSS dispersions are formed as stable aqueous systems enabling their use for deposition techniques such as inkjet printing.

Compared to other deposition techniques commonly used for the deposition of conductive polymers, like screen-printing and micro-contact printing, inkjet printing has its major advantages in being a digital, non-contact printing technique. Print pattern layouts can be generated in a fast and cost-effective process. Furthermore, the ability to deposit materials on-demand and even onto substrates with certain curvatures makes it very suitable for roll-to-roll processing.

The production of various devices, such as polymeric transistors[1] or all-polymer RC filters,[2] utilizing inkjet printing has already been demonstrated. However, when printing PEDOT-PSS dispersions with commercial inkjet printing heads, problems can occur like reduced printhead lifetime and low-quality drop formation. Especially a non-optimised inkjet printing performance with the presence of satellite drops could have serious consequences like electrical shorts in conductive tracks of electronic devices.

In this paper, an investigation of the parameters for high-quality drop formation and extended lifetime of the printhead when printing PEDOT-PSS ink with Xaar-type drop-on-demand inkjet printheads is presented. In addition, the conditions that influence the layer formation and conductivity of the printed films are evaluated. The application of this improved printing process for the production of PEDOT-PSS electrodes for a passive LCD device is shown.

Experimental

PEDOT-PSS dispersions were modified in different ways in order to achieve improved inkjet functionality and layer properties. For the printing of the adapted PEDOT-PSS dispersions Xaar's inkjet technology was employed, where modifications were made to the standard printheads aiming for improved performance and lifetime.

Xaar Drop-on-Demand Printheads

Piezoelectric drop-on-demand inkjet printheads from Xaar, which work on a shear-mode actuation principle, were employed in the present study. Figure 1 shows an XJ126-type printhead with 126 ink channels in a linear arrangement, which was used for the printing experiments. The 137 µm channel pitch of the printhead yields a printing resolution of 185 dpi (dots per inch) with the printhead mounted at 90 degrees against the scanning direction, while higher resolutions such as 309dpi can be achieved by inclining the printhead. Most experiments were performed with the XJ126/300 printhead model, which delivers typical drop volumes of 50 pl at repetition frequencies up to 7.5 kHz. Experimental prototype greyscale printheads with 5 grey-levels and sub-drop volumes of 3-4 pl were also utilized in this study.

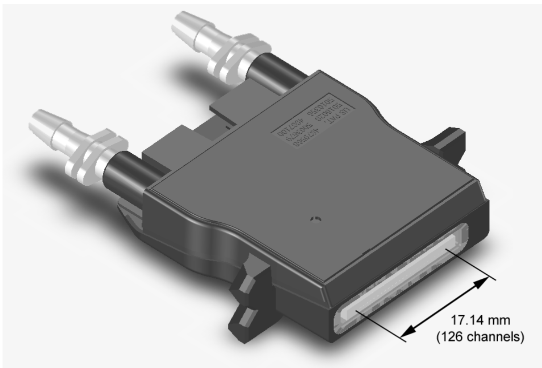

Figure 1. The XJ126 printhead model with 126 channels in a linear arrangement.

The principle of drop formation with Xaar-type printheads is based on the generation of an acoustic wave within the printhead actuator channel, which creates drop ejection through a well-defined nozzle.[3,4] This mode of operation is strictly non-thermal and is only based on the mechanical motion of the channel walls, thus minimizing the stresses on the printhead and the fluid.

As the PEDOT-PSS dispersions are based on aqueous systems and typically have a low pH value, an improved passivation coating was introduced on some of the development-type printheads used in this study. This coating consists of a Parylene layer on the channel walls and electrodes. To evaluate the quality of the drop formation with the PEDOT-PSS dispersions, printheads both with and without a non-wetting coating layer at the nozzle plate surface were tested.

Adaptation of PEDOT-PSS Dispersions for Inkjet

An aqueous Orgacon coating solution provided by Agfa was used as the principal PEDOT-PSS polymer dispersion. In this work the dispersion as received was subsequently adapted in several steps to improve its suitability for inkjet printing. The solid content of the dispersion was typically 1.2 wt%, which was slightly reduced during the ink formulation as described below.

The pH value of intrinsic PEDOT-PSS systems is around 2, which presents a problem in inkjet printing since the corrosive fluid could drastically shorten the lifetime of the printhead. In order to reduce the risk for corrosion effects, the polymer dispersion was adjusted to pH 6-7 by drop-wise addition of DMEA (dimethylethanolamide) during continuous magnetic stirring. The pH value was raised to the desired value and then measured and readjusted after 1-2 hours.

The PEDOT-PSS dispersion was typically diluted with 10 wt% (weight%) deionised water in order to obtain a more suitable viscosity for inkjet printing with Xaar-type printheads. Since the intrinsic polymer itself is a water-based dispersion this dilution has a minimal effect on the functionality of the polymer.

To further improve inkjet performance of the dispersion a low volatile co-solvent, i.e. ethylene glycol or glycerol, was added in different concentrations. The modified polymer dispersion was mixed and its surface tension then adjusted using a surfactant, Dynol 604 from Air Products. After addition of the surfactant the ink was heavily stirred for a few hours and left overnight. Finally the ink was filtered through a 1 μm syringe filter in order to remove larger particles and agglomerates that could clog the printhead filter and nozzles.

Characterization of PEDOT-PSS Ink Properties

Measurement of the viscosities of the different dispersions was performed using a PHYSICA UDS 200 rheometer. The measurements were carried out along a shear ramp in the shear-rate range of 50-2000 1/s. The rheogram of shear stress, τ, versus shear rate, γ, within the region of laminar flow (i.e. 50-800 1/s) was well-fitted by the Bingham approximation:

$$\tau = \tau_0 + \eta_{pl}\dot{\gamma} \tag{1}$$

to yield values for the plastic viscosity, η_{pl}, and yield stress, τ_0. For the unmodified Orgacon dispersion the result was τ_0 = 1.04 Pa and η_{pl} = 25.4 mPas. For the modified ink containing 30 wt% ethylene glycol and 10 wt% added water values of τ_0 = 0.66 Pa and η_{pl} = 22.2 mPas were obtained.

Equilibrium surface tension measurements were carried out using a Sigma 70 high performance tensiometer equipped with a Du Nouy ring. Inks that were adjusted using the surfactant Dynol 604 in concentrations from 0.004 wt% to 0.05 wt% were found to have surface tensions decreasing from 47 mN/m to 27 mN/m.

Inkjet Printing Experiments and Characterization

The functionality of the different PEDOT-PSS inks with the Xaar inkjet printheads was evaluated using a microscope rig with stroboscopic illumination, to visualise the ink droplets in flight. This test rig enables assessment of the quality and stability of drop formation, as well as the measurement of ink drop velocities and drop volumes.

Different test structures and patterns were printed on glass slides, in order to evaluate the print quality and the electrical properties of the printed PEDOT-PSS layers. Prior to printing the substrates were cleaned in a 5% Deconex solution for 5-20 minutes and rinsed rigorously in deionised water, then placed in a deionised water bath for another 5-20 minutes. Finally they were blown dry with nitrogen.

In test printing the substrates were placed on a heating element and preheated to approximately 80ºC, with this temperature maintained until the prints were visually dry.

The samples were then moved to an oven or heating plate and baked at typically 175ºC for 5-15 minutes.

The surface topography and thickness of the inkjet printed layers was measured using a ZYGO NewView 5010 profilometer, which is based on a white light interferometric measurement system. This system enables large area scans with a maximum lateral resolution of 0.88 µm for a 20× objective and a vertical resolution down to 0.1 nm.

Resistivity measurements were performed with commercial and home-built 4-point probes. Measurements were taken at several positions on a continuous layer, and averaged for further calculations.

Results and Discussion

Inkjet Printhead Functionality with PEDOT-PSS Inks

One of the main objectives of the present investigation was to identify the parameters for optimised printhead performance when printing PEDOT-PSS dispersions. The printhead functionality was evaluated with regard to drop formation and jetting reliability at high drop ejection frequencies, and in respect to maximised lifetime of the inkjet printhead.

Binary Xaar-type printheads usually require an ink viscosity of around 10 mPas. The PEDOT-PSS dispersions were found to show shear-thinning behaviour, fitting the Bingham approximation, and could thus be characterised in terms of their plastic viscosities given above. However, these steady-state viscosities can only be regarded as an indirect measure of the fluid properties at the extremely high rates of oscillatory shear present during drop generation within the inkjet nozzle. Experimentally, the viscosity of the PEDOT-PSS dispersions was found to be most suited when diluting the original Orgacon dispersion with 10 wt% deionised water.

The addition of the co-solvent ethylene glycol or glycerol did not result in a significant change in viscosity, and the printhead was generally found to function well for different concentrations of co-solvent. Furthermore, the addition of more than 5 wt% of co-solvent resulted in slightly improved drop formation, with less satellite drops and improved stability at higher frequencies. In particular, it increased the so-called decap time, i.e. the time the printhead can idle without giving problems to start up again. The best results for the inkjet printing performance in the stroboscopic test rig were found at ethylene glycol concentrations of 30 wt% or glycerol concentrations of 10 wt%.

Such optimised drop formation performance can be seen in figure 2. In this stroboscopic image ink droplets are shown in flight leaving the nozzle plate, ejected continuously from all channels of the printhead at the maximum drop firing frequency of 6.4 kHz. The composition of this PEDOT-PSS ink was 80 wt% Orgacon, 10 wt% glycerol, 10 wt% added water, with the addition of 0.025 wt% Dynol 604 surfactant. In this case the velocity of the drops was 6 m/s. The drops in flight were found to have only a variation of 1.1% in their positions at a distance of 2.4 mm from the nozzle plate. This low deviation shows the remarkably stable drop ejection with this adapted PEDOT-PSS ink. It is also notable that there are almost no satellite drops present at distances larger than 1 mm, which is the nominal printhead-substrate distance. This is of significance for printing of electronic structures, where the occurrence of satellite drops can cause shorting of circuits and malfunction of devices.

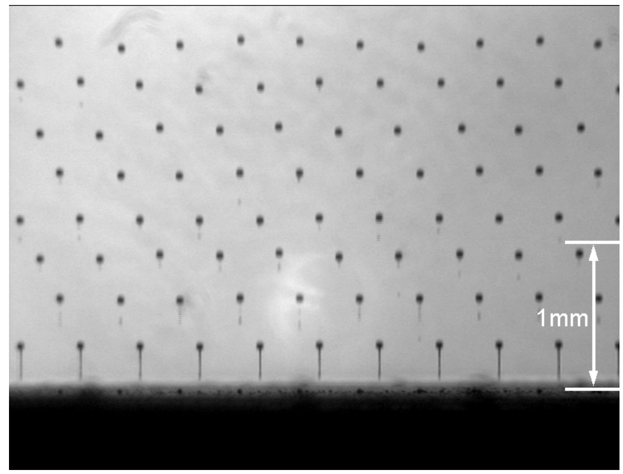

Figure 2. Inkjet drop formation with a well-adapted PEDOT-PSS ink at 6.4 kHz (drop speed = 6 m/s).

The effect of the added surfactant is to reduce the surface tension of the unmodified Orgacon solution, with a value of 71 mN/m, to the levels required for controlled inkjet printhead performance. Orgacon dispersions with 0.004 - 0.05 wt% added surfactant, with the corresponding surface tension values listed above, were generally found to be suitable for the Xaar inkjet printhead. The best performance was achieved at a concentration of 0.025 wt% surfactant, corresponding to a surface tension of 31 mN/m. The inks with a higher surfactant concentration of 0.05 wt% (surface tension of 27 mN/m) show slightly reduced jetting reliability at maximum firing frequencies. However, the surface tension also has a significant influence on the ink-substrate interaction, resulting in different spreading behaviour of printed ink drops. The large range of admissible surface tension values for the inkjet printing process thus allows the freedom to optimise layer formation on different substrates.

High quality inkjet printing performance as shown in figure 2 was achieved using a printhead with non-wetting coating on the nozzle plate surface. Without such a coating, increased instabilities in the drop firing performance were found, as well as higher angular deviation of the ejected droplets. In order to achieve optimised functionality it was also necessary to adapt the driving waveform of the printhead actuator for the aqueous PEDOT-PSS inks, which resulted in an increased length of the driving pulse.

As the lifetime of the inkjet printhead is an important issue, especially when printing corrosive fluids such as aqueous PEDOT-PSS dispersions, a preliminary lifetime test was performed. Two development-type printheads that have a Parylene passivation coating on the actuator channels and electrodes were compared to the performance of a standard XJ126/300 printhead model. An ink composed of pH-adjusted Orgacon (80%), glycerol (10%), added water (10%) and Dynol 604 (0.025%) was continuously ejected from the printheads at a firing frequency of 2 kHz. The ink was re-circulated in a closed system during the test. The initial test results were taken after 0.4×10^9 drops per channel, which corresponds to approx. 10% of the specified lifetime of the XJ126 printheads when used with approved oil-based or UV-curable ink. After this test duration the standard XJ126/300 printhead had about 5-10% channels with reduced performance, i.e. missing drops or lower drop speed. One of the two Parylene coated printheads, however, was fully functional after this test. The second one had two channels with lower drop speed, which indicated the onset of corrosion effects on one channel wall. The Parylene coating in these printheads was not optimised, thus it should be expected that further improvement of this coating could further extend the lifetime.

Properties of Inkjet Printed PEDOT-PSS Layers

The inkjet printed PEDOT-PSS layers were characterised with regard to achievable structural geometries and dimensions, and for best electrical properties of the printed films.

The dimensions of the printed pattern are mainly determined by the spreading of the ink drops after impacting the substrate, which is determined by the substrate's surface chemistry and temperature. For the glass substrates utilized in this work the best resolution of features was achieved when cleaning the substrates with Deconex, as described above, and maintaining a temperature of 80ºC during printing. For lower substrate temperatures the ink spreading was more substantial, and the control of fine structure dimensions was thus difficult.

Figure 3 shows a profilometer image of an electrode pattern printed at these substrate conditions. For this pattern the ink contained Orgacon (85%), glycerol (5%), added water (10%) and Dynol 604 (0.025%). The surface profile in the figure shows the sharpness of the pattern edges formed, even if there are still variations in layer thickness present.

Further parameters influencing the pattern formation on the substrate are surface tension of the PEDOT-PSS ink as well as the concentration of the co-solvent ethylene glycol or glycerol. Lower surface tension of the ink facilitates drop spreading and the formation of continuous lines on the substrate. However, the surface tension must be adapted to the various substrate conditions, within the range suited for inkjet printing.

The content of the co-solvent was found to have an influence on the uniformity in thickness of the inkjet printed layers. The ranges of 5-20 wt% glycerol or 5-15 wt% ethylene glycol were identified to be most suitable for uniform layer thickness. At higher ethylene glycol contents a thicker rim formed at the structure edges, with thickness increasing with increasing concentration of this co-solvent.

Figure 4 shows a profilometer image of lines printed at 720dpi with approx. 3 pl drop volumes from a prototype greyscale printhead. The line width achieved with this printhead is in the order of 40 µm, with a line thickness of 15 nm, as seen in the surface profile image taken of one of the lines. This can be compared to a width of approximately 150 µm for lines printed with a binary XJ126/300 printhead.

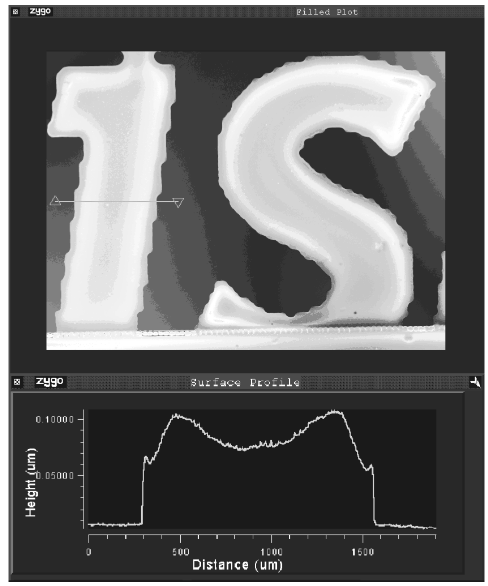

Figure 3. Profilometer scan of an inkjet printed PEDOT-PSS electrode pattern (scan area = 6.17 × 4.63 mm).

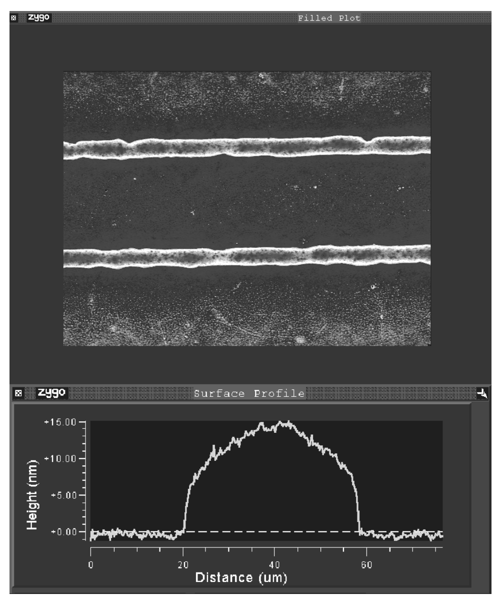

Figure 4. Profilometer topography map of PEDOT-PSS lines inkjet printed with a greyscale printhead, having 3 pl drop volume.

It was found that the addition of high boiling point solvents to PEDOT-PSS dispersions considerably improved the electrical conductivity of the film produced. A proposed explanation for this phenomena is the re-arrangement of the polymer-chain structures during drying combined with re-dissolution of the PSS-rich surface layers at the grain boundaries.[5]

In this work the electrical properties of the inkjet printed PEDOT-PSS layers were evaluated as a function of the amount of the co-solvents ethylene glycol and glycerol in the ink. The sheet resistance was measured with a 4-point probe on single-pass inkjet printed PEDOT-PSS layers. Taking the layer thickness into account, the conductivity can be plotted versus the solvent content, as shown in figure 5. High conductivity values of up to 120 S/cm could be achieved with glycerol concentrations higher than 5 wt%, and with ethylene glycol concentrations of at least 7.5 wt%.

It should be noted that this window of fluid compositions resulting in highest conductivity largely coincided with the compositions giving best inkjet printing performance and layer formation.

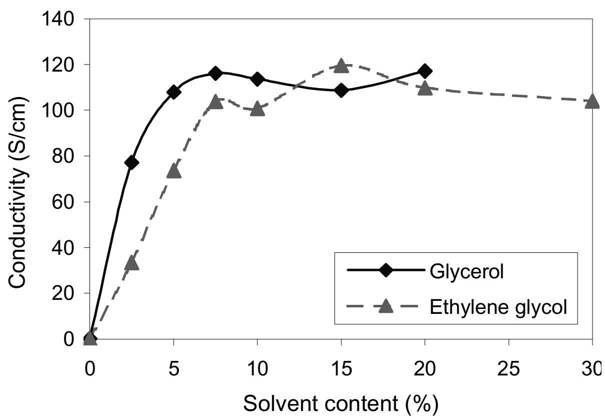

Figure 5. Conductivity of single-pass inkjet printed PEDOT-PSS films as a function of co-solvent type and amount.

Application Example: Passive LCD Device

For liquid crystal displays (LCD), PEDOT-PSS is an interesting alternative as electrode material. Normally indium tin oxide (ITO) is used, which is a transparent metal oxide with relatively high conductivity in the order of 15000 S/cm. ITO is deposited in vacuum with vapour deposition or sputtering techniques. PEDOT-PSS thus has potential advantages in mechanical and processing properties, for example in its ability to be applied with spin coating or inkjet printing. The main drawbacks for using PEDOT-PSS are its low conductivity, on the order of 1-150 S/cm, and its optical absorption. Figure 6 shows the optical transmission of PEDOT-PSS and ITO on glass substrates. PEDOT-PSS has a higher absorption that also gives a slight blue shift to the LCD display. It should be noted that these values could be increased by minimizing the reflections, using e.g. hard coat layers. Another potential problem with the conducting polymer could be its chemical stability, with degradation and decomposition resulting in a decreased conductivity.

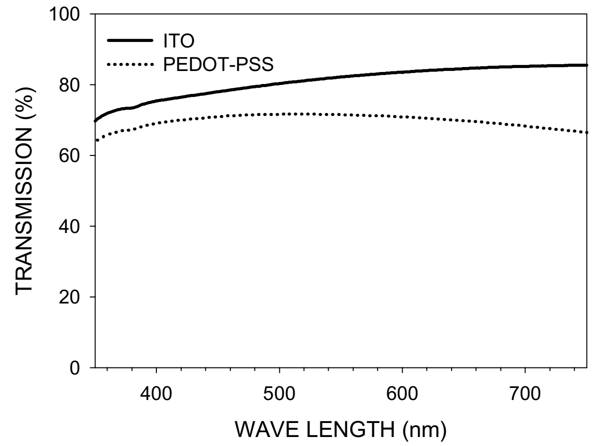

Figure 6. The optical transmission of ITO and PEDOT-PSS coated glass.

Figure 7 shows a prototype LCD in the off and on states. The prototype display was built on a glass substrate and an adapted PEDOT-PSS material was inkjet printed as electrode. The Orgacon PEDOT-PSS dispersion was mixed with 10 wt% glycerol and 10 wt% water, with addition of 0.025 wt% Dynol604. The conductivity of the layers produced with this ink was found to be approx. 120 S/cm. The thickness of the PEDOT-PSS layer for the LCD electrodes, which was produced in two printing passes, was measured at 180 nm, giving a sheet resistance of around 450 Ω/□. This value can be compared with the normal values for ITO substrates where the surface resistance is around 10 Ω/□. For alignment of the liquid crystal a photoactive material was used. In LCD manufacturing, mechanically rubbed polyimide is normally used as the alignment layer. In that case, polyimide is applied in a precursor form that is imidized by heating to 250°C. This high processing temperature could affect the conductivity of the PEDOT-PSS layer by thermal decomposition. An alternative means to avoid the need for high temperature curing is to use photoactive material as the alignment layer. Here the molecules or polymers in the photoactive material are ordered by polarized UV-light.

The switching voltage was compared for two displays, one using PEDOT-PSS and one reference display using ITO. Both displays had a cell gap of 8μm. The turn-on voltage for the PEDOT-PSS cell was 1.8 V, whereas the ITO reference cell had a turn-on voltage of 1.2 V. This difference could be due to the higher surface resistance of the PEDOT-PSS electrode. At a voltage of 5V the switching times of the PEDOT-PSS cell were 36.5 ms and 61.0 ms for turn-on and turn-off. For the ITO cell these values were 24.0 ms and 78.3 ms, respectively.

The main drawback of the prototype display is the high light absorption of the PEDOT-PSS, as seen in figure 7. If the display is used in reflective normal white mode, the electrode pattern will be clearly visible. By using the display with backlight mode this effect will be reduced, and by using it in a normal black mode with backlight, the PEDOT electrodes are not visible. The next issue to study is the stability of the polymer, as this could present a problem for its use in commercial displays. The interactions between PEDOT-PSS, the hard coat and the liquid crystals also require further study.

Figure 7. A prototype LCD, with inkjet printed PEDOT-PSS electrodes, in the off and on states.

Conclusions

PEDOT-PSS dispersions have been successfully adapted for a high quality inkjet printing performance with Xaar-type piezoelectric inkjet printheads. This has been accomplished by adding a suitable surfactant and co-solvents such as glycerol and ethylene glycol. These modifications also improved the layer formation and conductivity of the inkjet printed structures, and high conductivities of inkjet printed films up to 120 S/cm could be achieved. It has been found that the PEDOT-PSS ink compositions for optimised layer properties also largely match with the range where best inkjet performance could be achieved. Additionally, the quasi-neutral pH values of the adapted PEDOT-PSS dispersions reduce corrosion effects within the printhead and increase the printhead lifetime.

A passive LCD device that incorporates inkjet printed PEDOT-PSS electrodes was built. Even if the higher optical absorption of the PEDOT-PSS electrodes is currently a drawback, it could be shown that the switching times of an LCD cell with PEDOT-PSS electrodes are nearly comparable to the switching times of an LCD with standard ITO electrodes.

Acknowledgements

The authors gratefully acknowledge Agfa for providing the Orgacon coating solution used in this work. We are also thankful to the Engineering Materials Physics group (Tmfy) at the Royal Institute of Technology (KTH), Stockholm, for access to electrical characterisation facilities.

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Biography

Wolfgang Voit is member of the Technology Department at Xaar. He has worked for the past 7 years on both inkjet printhead technology as well as on developing new applications of inkjet printing. He received his diploma from the University of Applied Sciences in Regensburg, Germany, in 1996. Wolfgang Voit is presently finalizing his PhD thesis on inkjet printing of magnetic and functional devices at KTH (Royal Institute of Technology), Stockholm.